

Catalytic activity of polyaniline/MnO₂ composites towards the oxidative decolorization of organic dyes

Ali H. Gemeay^{*}, Rehab G. El-Sharkawy, Ikhlas A. Mansour, Ahmed B. Zaki

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

Received 18 September 2007; received in revised form 15 November 2007; accepted 20 November 2007

Available online 22 November 2007

Abstract

The kinetics of the oxidative reaction of the textile dyes: direct red 81 (DR-81), indigo carmine (IC), and acid blue 92 (AB-92) with H₂O₂ in the presence of polyaniline (PANI)/MnO₂ composites has been investigated. Experiments were carried out in batch reactor under pseudo-first order conditions with respect to the [dye]. Effects of the preparation conditions of the composites on the reaction rate have been investigated. Among these conditions are [aniline], [acid], type of acid, mass of β-MnO₂, polymerization time, and annealing temperatures. At fixed [dye], [H₂O₂], and mass of composite, the rate constants increased upon increasing (i) the doping ratio of PANI, (ii) the percentage of PANI content, (iii) the degree of crystallinity of PANI, and (iv) the molecular weight of PANI. The presence of MnO₂ counterpart kept the medium at pH range (3–4) via adsorption of H⁺. The oxidation rate was enhanced with the increase in the initial concentration of H₂O₂, attained a maximum at 0.01 M and thereafter decreased. In contrast, the rate was inhibited with the increase in the initial dye concentration, and the pH. The activation parameters were determined. From the isokinetic relationship it was concluded that the catalytic reactions are entropy controlled. A reaction mechanism involving electron transfer from H₂O₂ to the PANI counterpart has been proposed. These results demonstrate that the PANI/MnO₂–H₂O₂ catalytic system may be envisaged as a method for the treatment of colored wastewaters.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Polyaniline composites; Catalyst; Decolorization; H₂O₂; Textile dyes; Kinetics

1. Introduction

Polyaniline (PANI) is one of the most promising candidates for industrial applications. It is easy to synthesize via simple chemical or electrochemical oxidation methods of aniline. The demand for materials possessing combination of wide range of desirable properties is always increasing. One of the techniques to develop such materials is the formulation of composites from compatible materials individually possessing the desirable properties. PANI blends and composites have been prepared mostly via the chemical oxidation route, although the electrochemical synthesis was also employed in some cases [1,2].

Inorganic nanoparticles such as CdS and CuS [3], clay [4], maghemite [5], MnO₂ [6], TiO₂ [7], and ZrO₂ [8] are used for the preparation of PANI nanocomposites. The interactions of PANI with these nanoparticles are reported to be via physical

adsorption or electrovalent bonding. PANI-grafted silica nanoparticles has been prepared by the in situ chemical oxidation of aniline using (NH₄)₂S₂O₈ by dispersion polymerization method [9]. It was found that MnO₂, PbO₂, and NH₄VO₃ particles can act as oxidants for the polymerization of aniline [10]. These oxidant ions (Mn⁴⁺, Pb⁴⁺ and V⁵⁺) are recoverable, recyclable, and have advantages over other conventional oxidants such as (NH₄)₂S₂O₈. In our previous studies, we reported the preparation and characterization of PANI/MnO₂ composites [11,12]. The parameters that have effects on the composition and thermal stability of the resulting composites were investigated.

PANI-modified electrodes have been employed for the oxidation of hydrogen [13], methanol [14], ascorbic acid [15], inorganic redox couples such as Fe²⁺/Fe³⁺ [16], and oxygen reduction [17]. PANI-supported vanadium complexes catalyzed the oxidation of alcohols to aldehydes and ketones with molecular oxygen [18]. Moreover, Fe(II), Co(II), and Mn(II) porphyrins supported on PANI have been used as catalysts in co-oxidation of styrene and isobutyric aldehyde [19]. PANI/

^{*} Corresponding author. Fax: +20 40 3350804.

E-mail address: agemeay@yahoo.com (A.H. Gemeay).

CuCl_2 and PANI/FeCl_3 transition metal complexes were found to be effective catalysts in the dehydrogenation oxidation of cinnamyl alcohols and mandelic acid [20].

The removal of dyes from industrial effluents received much attention as government legislation becoming increasingly stringent. Effluents from textile industry commonly contain high concentrations of organic and inorganic chemicals. These chemicals can extremely damage the environment if improperly disposed [21,22]. The worldwide annual production of the dyestuffs amounts to more than 7×10^5 t [23]. In view of their chemical structure, dyes can be classified as azo dyes, triarylmethane dyes, anthraquinone dyes, heterocyclic dyes, and phthalocyanine dyes. Over 15% of the overall dyes production is lost during manufacturing and application processes [24]. The majority of these dyes are either toxic or mutagenic and carcinogenic [25], and have potential health hazard to all forms of life [26].

An attractive, sludge free alternative method for the treatment of organic pollutants present in wastewater, including synthetic dyes is called advanced oxidation processes (AOPs). Hydroxyl radicals generated in sufficient quantities by AOPs, have the ability to oxidize the majority of organic pollutants present in the wastewater effluents [27,28]. Chemical oxidation technologies using oxidizing agent such as H_2O_2 exhibited lower degradation rates compared with the processes based on the generation of free radicals [29–31]. Addition of catalysts to the systems containing H_2O_2 leads to the generation of HO^\bullet with redox potential of 2.33 eV. These radicals exhibited faster rates for the degradation reaction compared with those of

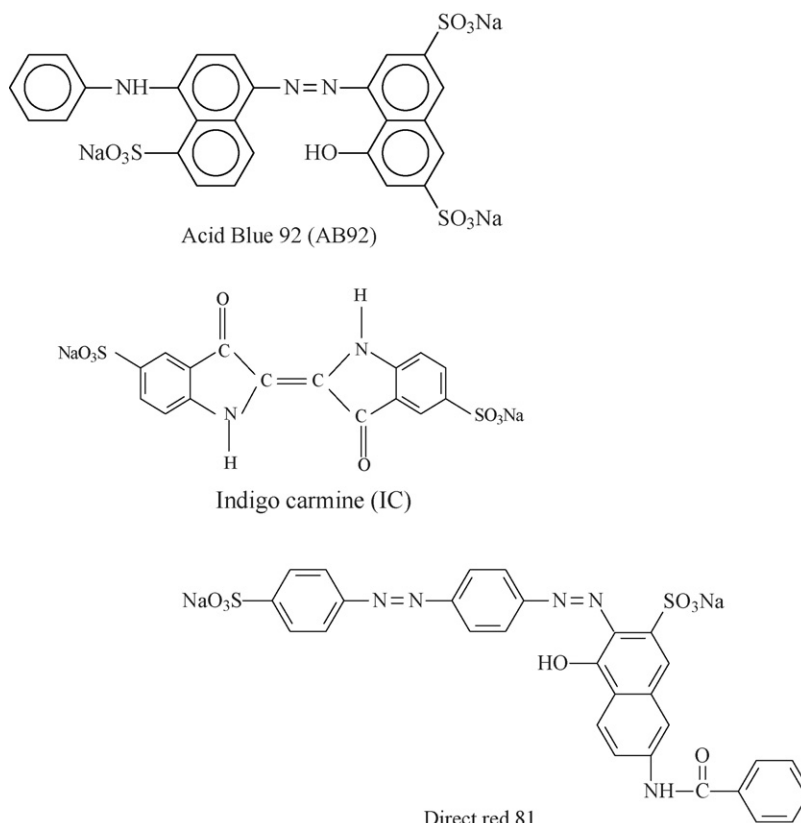
conventional oxidants [32–39]. In many cases catalyst separation is technically and/or economically unfeasible. Many active homogeneous catalysts including transitional metal ions and their complexes are toxic thus are potential environmental problem. Under these circumstances, it is desirable to develop heterogeneous catalytic system where the catalysts are easily separable.

This work is designed to better understanding the effect of preparation conditions of PANI/MnO_2 composites on the kinetics of the oxidative degradation of the target dyes with H_2O_2 . The influence of the kinetic variables was also considered in order to verify the optimum conditions for the facile oxidation of these dyes. This heterogeneous catalytic system has potential advantages of simple and inexpensive mass production of composites with a good thermal stability.

2. Experimental

2.1. Materials

Aniline was distilled under reduced pressure and stored in the dark below 4°C . Pure $\beta\text{-MnO}_2$ (99%, Riedel de Haen) having specific surface area $20\text{ m}^2\text{ g}^{-1}$ was used as received. Hydrogen peroxide (30% (w/v), Merck) was used. The initial concentration of H_2O_2 was determined iodometrically using standard $\text{Na}_2\text{S}_2\text{O}_3$. Acid blue 92 (C.I. 13390), 4-hydroxy-5-[[4-(phenylamino)-5-sulfo-1-naphthyl] azo]-2,7-naphthalene disulfonic acid trisodium salt, direct red 81 (4-[*p*-aminophenylazo] benzene sulfonic acid *N*-benzoyl acid), and indigo



Scheme 1.

carmines (disodium salt of 3,3-dioxobi-indolin-2,2-ylidene-5,5-disulfonate) were obtained from Aldrich. The structural formulas of these dyes are shown in Scheme 1.

2.2. Preparation of composites

PANI/MnO₂ composites were prepared according to the procedure reported in our previous works [11,12]. The composites were characterized using SEM, X-ray, FT-IR, TGA, zero point of charge, and magnetic susceptibility.

2.3. Kinetic measurements

The kinetic measurements were carried out using UV/visible Shimadzu-2100S recording spectrophotometer. It is equipped with a thermo-electrically temperature controlled cell holder (TCC-260) at high accuracy over temperature range 7–60 °C. The UV-lamp (Vilber Lourmat, 2 × 6 W, 254 nm tube, Philips) was used as UV-irradiation source in the experiments where the effect of UV-irradiation was investigated. For pH measurements, Crison pH-meter digit-501 that had been calibrated prior to the measurement was used.

In typical kinetic run, a number of reactors (100 ml) containing a definite quantity of the solid composite together with the appropriate volume of distilled H₂O were placed in a water shaker thermostat in order to attain the desired temperature. To each reactor 1 ml of the separated thermostatted dye and H₂O₂ solutions were added and zero time was noted. At regular time intervals aliquots of each reactor were withdrawn and the absorbance was recorded at the corresponding λ_{max} of each dye. In the absence of the composite, the dye/H₂O₂ mixture was stable for several hours without any noticeable change in the absorbance of dyes, which indicates that there was no reaction takes place between the dye and H₂O₂.

2.4. Stoichiometry

Since the oxidative degradation of the organic dyes can convert organic carbon into CO₂. It has been reported that the mineralization of IC was accompanied by releasing of CO₂, SO₄²⁻, NH₄⁺ and NO₃⁻ ions [33,40]. Thus, in closed fitting system and by using CO₂-free distilled water, 100 ml of 10⁻³ M of dye solution was allowed to react with 100 ml of 0.5 M of H₂O₂ in the presence of 0.5 g of composite (III). The CO₂ was trapped by Ca(OH)₂ solution and the precipitated CaCO₃ was determined gravimetrically. After complete color removal the mixture was filtered off and the unreacted H₂O₂ was determined iodometrically. Our finding indicated that about 60% of dye carbons were transformed into CO₂. The difference between the measured and theoretical is probably due to the existence of some intermediate products or loss of CO₂. The sulfate ions were determined gravimetrically by the precipitation into BaSO₄ using BaCl₂ solution [23,33–35]. The total acid concentration in the mixture was determined by titration with NaOH and the concentration of HNO₃ was estimated by difference.

3. Results and discussion

3.1. Variation of PANI/MnO₂ composition

Several parameters have been varied during the preparation of PANI/MnO₂ composites in order to establish the optimum conditions to obtain composites having high catalytic activity. Among these parameters are (i) [ANI], (ii) [acid], (iii) acid type, (iv) the mass of β -MnO₂, (v) polymerization time and (vi) polymerization temperature. The parameters and the abbreviation number of each resulting composite are listed in Table 1.

Table 1

Summarizing the preparation conditions of the PANI/MnO₂ composites and their abbreviations cited in the text

The varied parameter	Composite number	$k \times 10^{-2} \text{ s}^{-1}$ (pgdc)		
		DR-81	AB-92	IC
[ANI] (M) ^a				
0.43	I	8.75	7.93	11.1
0.54	II	9.66	9.05	12.3
0.64	III	7.20	10.8	13.4
0.76	IV	22.6	12.7	16.5
0.87	V	31.2	14.9	18.1
0.96	VI	39.8	17.5	20.6
β-MnO ₂ (g) ^b				
1.0	VII	5.89	3.27	9.35
1.5	VIII	10.3	6.56	11.3
2.5	VIII	15.8	12.5	15.3
3.0	X	17.2	16.0	16.2
4.0	XI	24.7	18.4	19.4
[H ₂ SO ₄] (M) ^c				
0.57	XII	10.7	7.19	5.39
0.64	XIII	11.8	9.98	8.54
0.76	XIV	16.4	13.9	17.6
0.95	XV	14.9	12.4	15.6
1.33	XVI	9.75	6.22	10.4
1.52	XVII	8.20	5.79	5.06
H ₃ PO ₄ ^d	XVIII	0.53	0.57	0.44
HCl ^d	XVIII	28.0	7.40	11.2
HNO ₃ ^d	XX	41.2	12.9	21.5
4 h ^e	XXI	15.9	11.7	14.8
10 h ^e	XXII	20.0	12.4	18.3
17 h ^e	XXIII	24.3	15.8	24.6
24 h ^e	XXIV	28.3	22.3	30.2
$t = 5^\circ \text{C}^f$	XXV	40.5	12.8	27.8

k is determined for the reaction carried out using 0.007 M H₂O₂ and [dye] = 1×10^{-4} M, 0.02 g of the composite.

^a Preparation condition: β -MnO₂ = 2 g, [H₂SO₄] = 1.15 M, $t = 25^\circ \text{C}$ and polymerization time = 1 h.

^b Preparation condition: [ANI] = 0.64 M, [H₂SO₄] = 1.15 M, $t = 25^\circ \text{C}$ and polymerization time = 1 h.

^c Preparation condition: [ANI] = 0.64 M, β -MnO₂ = 2 g, $t = 25^\circ \text{C}$ and polymerization time = 1 h.

^d Preparation condition: [ANI] = 0.64 M, β -MnO₂ = 2 g, [acid] = 1.15 M, $t = 25^\circ \text{C}$ and polymerization time = 1 h.

^e Preparation condition: [ANI] = 0.64 M, β -MnO₂ = 2 g, [H₂SO₄] = 1.15 M and $t = 25^\circ \text{C}$.

^f Preparation condition: [ANI] = 0.64 M, β -MnO₂ = 2 g, [H₂SO₄] = 1.15 M and polymerization time = 1 h.

Direct red 81 (DR-81), indigo carmine (IC), and acid blue 92 (AB-92) dyes were chosen as a model to study the catalytic activity of PANI/MnO₂ composites. When the solution of individual dye was mixed with H₂O₂ in absence of the composites, no change in the absorption spectrum of the dye was observed. Moreover, when the dye solution was mixed with H₂O₂ in the presence of solid MnO₂, again no change in the absorption spectrum was observed. When the catalysts (PANI/MnO₂ composites) were added, the reaction was started. A gradual decrease with time in the absorbance at $\lambda_{\text{max}} = 508$, 571, and 610 nm of the corresponding dyes DR-81, IC, and AB-92, was observed (Fig. 1). The kinetic studies were carried out under pseudo-first order conditions with respect to [dye], where the initial concentration of hydrogen peroxide, [H₂O₂], was at least 10-fold excess over [dye]. The rate constant, k_0 was determined from the slope of the first-order plots shown in Fig. 2, which verify Eq. (1). A_t is the absorbance at time t and A_0 is the absorbance at $t = 0$, w is the amount of the composite, and k_0 is the observed rate constant.

$$\ln A_t = \ln A_0 - k_0 t, \quad (1)$$

values of k (specific rate constant) per gram of dry composite (pgdc) were determined from the relation $k = k_0/w$ and are listed in Table 1.

3.1.1. Effect of [ANI]

The catalytic activity of PANI/MnO₂ composites prepared with variable aniline concentrations has been investigated. These composites (I–VI) have been tested individually via the reaction with the probe dye. A typical kinetic run was carried out under the conditions: [dye] = 1×10^{-4} M, [H₂O₂] = 7×10^{-3} M, 0.02 g of the composites, and at 30 °C. Values of k , were determined from the corresponding first-order plots and are listed in Table 1. The dependence of k upon [ANI] is depicted in Fig. 3. This figure shows two

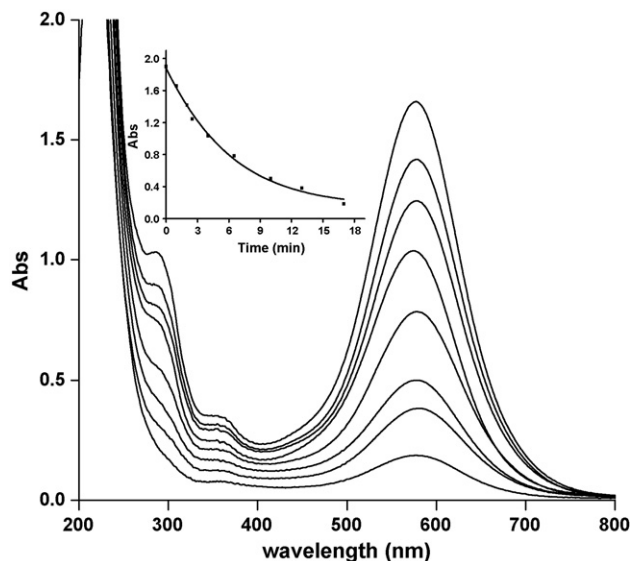


Fig. 1. Time resolved absorption spectra of the reaction of AB-92 (1×10^{-4} M) with of H₂O₂ (7×10^{-3} M) in the presence of 0.02 g of the composite (III) at 30 °C.

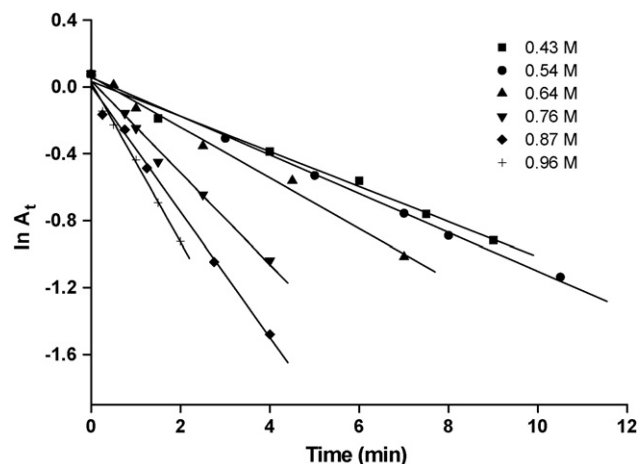


Fig. 2. First-order plots for the reaction of DR-81 (1×10^{-4} M) with H₂O₂ (7×10^{-3} M) in the presence of 0.02 g of the composites (I–VI) at 30 °C.

characteristic stages for each individual dye. It demonstrates that k is directly proportional to [ANI] in both stages. Below [ANI] $\cong 0.65$ M the slopes have the values: 0.19, 0.14, and 0.11, for DR-81, AB-92, and IC, respectively. Above [ANI] $\cong 0.65$ M the slopes have the values: 0.80, 0.21, and 0.22 for the same order of dyes. This means that DR-81 is the most degradable dye, while IC is the lowest one. Moreover, when k is plotted against the molar ratio (r) of ANI/MnO₂, again two characteristics stages are obtained and are intersected at $r \cong 1.4$ (data not shown). It was observed that at low [ANI] a long induction period was noticed, while at high [ANI] the polymerization reaction started immediately. These results may be explained on the basis of the following aspects: (i) the PANI content in the resulting composites increases with increasing [ANI]. The evidence for that comes from the TAG analysis. TAG revealed that PANI content is increased by about 13% when [ANI] increased from 0.58 M to 0.85 M, (ii) increasing the molecular weight of PANI [11,12]. Again, from TGA analysis, the highest decomposition temperatures have the values: 500 °C, 500 °C, and 450 °C, for the composites prepared with [ANI] of 0.85 M, 0.64 M and 0.53 M, respectively. This is in good agreement with that found elsewhere where the low molecular weight is released at lower

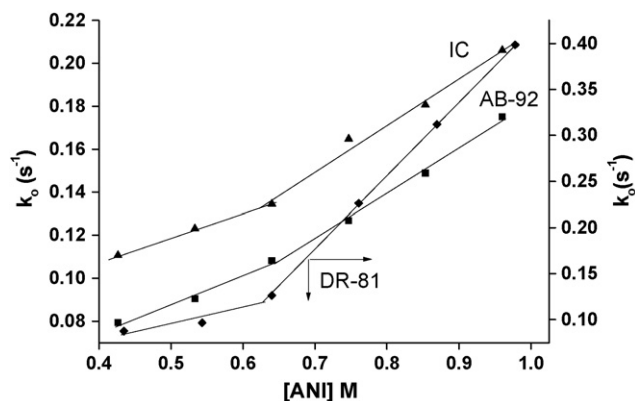


Fig. 3. The relationship between [ANI] and the rate constant for the reaction of the chosen dyes in the presence of the composites (I–VI).

temperature [41]. Thus, PANI formed with $[ANI] > 0.64$ M has higher molecular weight compared with PANI formed with $[ANI] < 0.64$ M. (iii) Increasing the doping ratio of PANI. To confirm which forms of PANI (emeraldine base, EB or emeraldine salt, ES) is the active catalyst in our system, a kinetic run was carried out using PANI/MnO₂ composite which is previously treated with NH₄OH, i.e. formation of deprotonated form (EB) of PANI. The run showed no catalytic reaction. This is good evidence that the active form of PANI in the present system is the protonated form of PANI (ES). (iv) XRD analysis revealed that the highly crystalline composite is formed at high $[ANI]$ [11,12]. This means that the catalytic activity of the composites is dependent on the doping ratio and the degree of crystallinity. It has been reported that the high catalytic activity of PANI toward dehydrogenative oxidation reaction of benzylamine was attained at high doping ratio [42]. Therefore, the existence of the break point in Fig. 3 may be attributed to the drastic increase in the molecular weight, the doping ratio, and the degree of crystallinity of PANI.

As shown in Table 1 when the type of dye is changed while the other kinetic experimental conditions are kept constant, the values of k follow two sequence orders depending on the $[ANI]$ range. In the range 0.43–0.64 M, the k values have the order: IC > DR-81 > AB-92. In the range 0.64–0.96 M, the k values follow the order: DR-81 > IC > AB-92. It is clear that in both orders the lowest k is observed for AB-92. This may be due to the following: (i) the structure of AB-92 contains two naphthyl moieties compared with the other two dyes. The DR-81 has one naphthyl moiety, while IC has not. Of course, naphthyl moiety is difficult to degrade compared with phenyl or heterocycle rings present in DR-81 and IC and (ii) the difference in the chromophoric groups of these dyes. DR-81 contains two azo groups: AB-92 has one azo group, while IC is free of such group.

3.1.2. Effect of the amount of β -MnO₂

The influence of the amount of β -MnO₂ used during the preparation of PANI/MnO₂ composites (VII–XI), Table 1, has also been studied. Values of k determined from the first-order plots are listed in Table 1. As shown in Fig. 4, it is clear that k values increased with increasing the amount of β -MnO₂ up to 2.5 g, and almost a limited increase is attained at higher

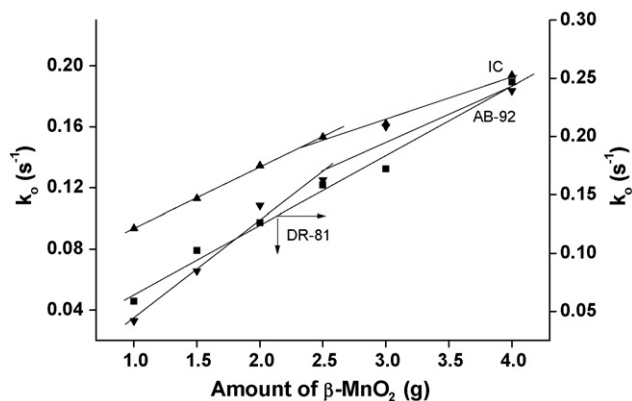


Fig. 4. The relationship between the amount of MnO₂ and the rate constant for the three dyes.

amounts of the oxide. Moreover, when k is plotted against the molar ratio $[Ox]/[ANI]$, the same trend is obtained. These results may be ascribed to the following: (i) FT-IR spectral analysis shows that the composites prepared at high amounts of oxide have high acidic characters due to (a) adsorption of H⁺ on the surface of the oxide, (b) formation of H-bonding between the hydroxyl groups on the surface and the amine, imines nitrogen of the PANI and (c) transformation of MnO₂ into MnOOH. (ii) XRD analysis revealed that increasing the MnO₂ leads to an increase in the degree of crystallinity of the produced composites, which is attributed to the increase in PANI content and the doping ratio. (iii) From TGA analysis, the highest decomposition temperature, T_m has the values: 570 °C, 500 °C, and 400 °C, for the composites prepared with 4 g, 2 g, and 1 g of MnO₂, respectively. Again, this sequence agrees with the order of % PANI content of the composites.

The increases in k values observed at high amounts of MnO₂ may be assigned to the low percentage of PANI content in the composites compared with the percentage of MnO₂. With respect to the variation of dyes, as shown in Table 1, the value of k at MnO₂ < 2.5 g follows the order: IC > DR-81 > AB-92, while at MnO₂ > 2.5 g the rate constant follows the order: DR-81 > IC > AB-92.

3.1.3. Effect of $[H_2SO_4]$

The effect of $[H_2SO_4]$ used during the polymerization reaction, on the catalytic activity of the resulting composites has been investigated. As shown in Fig. 5, the rate constants increased with increasing $[H_2SO_4]$ attaining a maximum at $[H_2SO_4] \cong 0.76$ M and thereafter decreased. It has been reported that the high [acid] results in high extent of the anilinium cation formation as intermediate, which plays significant role in favoring rapid transformation of ANI into PANI [43]. Thus, the yield of PANI increased with increasing $[H_2SO_4]$ until ca. 0.76 M. While for solutions of $[H_2SO_4] > 0.76$ M, the degradation of the formed PANI takes place and consequently low yield is produced. Similar behavior has been reported [44]. The degradation mechanism of PANI is attributed to either the

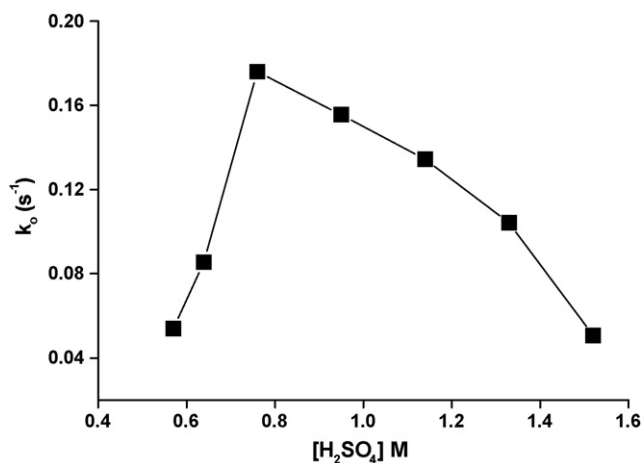


Fig. 5. Variation of k , with $[H_2SO_4]$ for the reaction of IC (1.0×10^{-4} M) with H₂O₂ (7×10^{-3} M) in the presence of 0.015 g of composites (XII–XVII) at 30 °C.

formation of soluble quinone–hydroquinone structures or to the formation of over-oxidized polymer [45,46].

3.1.4. Effect of various acids

PANI/MnO₂ composites have been prepared in the presence of different acids like H₂SO₄, HNO₃, HCl, and H₃PO₄. The catalytic activity of each individual composite was tested. Values of the corresponding k were determined from the first-order plots and are listed in Table 1. The values followed the order: HNO₃ > H₂SO₄ > HCl > H₃PO₄ for the reactions with IC and AB-92, while for the DR-81 the order is HNO₃ > HCl > H₂SO₄ > H₃PO₄. The order of k in case of IC and AB-92 is similar to the order of the weight loss of the second step, doping anions loss, determined from TGA analysis. It was found that the weight loss of doping anions follows the order NO₃[−] > HSO₄[−] > Cl[−] > H₂PO₄[−] with the values 16.54%, 10.04%, 7.95%, and 4.95%, respectively [12]. This is consistent with the percentage of PANI in the corresponding composite. The adsorption of the present anions on MnO₂ surface has been reported elsewhere [47]. It has been found that the conductivity of PANI prepared with different acids follows the order PANI/Cl[−] > PANI/HSO₄[−] > PANI/H₂PO₄[−] [48]. The minor deviation observed in the order of k for the reaction of DR-81 may be attributed to the difference in chemical structure of the dyes.

3.1.5. Effect of polymerization time

The influence of the polymerization time of the composites on the catalytic activity has been considered. From Table 1, it is clear that increasing the stirring time leads to an increase in k values. TGA analysis showed that the percentage of PANI was 51.77%, 68.58%, and 82% for the composites prepared at 1 h, 4 h, and 10 h, respectively. It has also been reported that long polymerization time is essential to obtain high-molecular weight PANI [49]. Jin et al. reported that the stability of PANI was significantly improved by increasing the time of polymerization [50].

3.1.6. Effect of polymerization temperature

The temperature at which the polymerization reaction occurred is one of the important factors that control the macromolecular properties of PANI, namely, its molecular weight and doping ratio. To verify this phenomenon, two composites were prepared at 5 °C and 25 °C and their catalytic activities were investigated. Table 1 indicates that the rate constant of DR-81, AB-92, and IC was enhanced by about 68.8%, 15.2%, and 51.7%, respectively, when the catalytic reactions were carried out with the PANI/MnO₂ composite prepared at 5 °C. It has been reported that the molecular weight of PANI was increased with decreasing the polymerization temperature. Moreover, the polymer prepared at low temperature has high molecular weight which is associated with better mechanical properties compared with that prepared at high temperature [51].

3.1.7. Effect of annealing of the composites

Thermal stability of PANI composites has received considerable attention because of its potential applications.

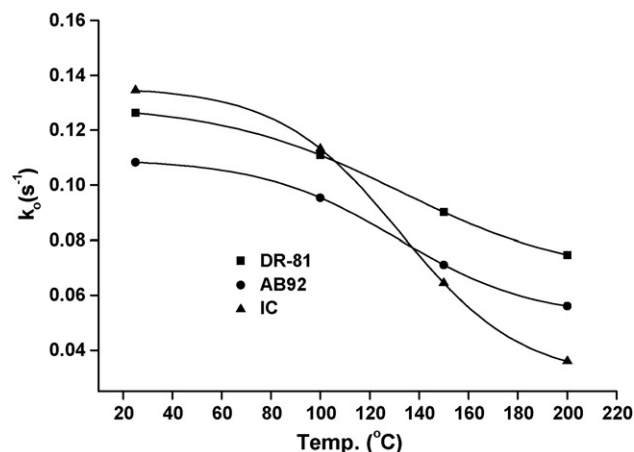


Fig. 6. Dependence of the rate constant on the annealing temperature.

Composite (III) was annealed at 100 °C, 150 °C, and 200 °C in ambient air for 3 h. The annealed composite was employed as catalyst for the oxidation reaction. Fig. 6 shows the dependence of the rate constant on the annealing temperatures. This behavior may be interpreted on the basis that the annealing process causes several chemical transformations. Among these are (i) slight dedoping takes place due to the evaporation of dopant anions, (ii) oxidation of the polymer backbone due to the presence of air oxygen and (iii) the loss of moisture. The former two factors may be responsible for lowering the catalytic activity of the annealed composite. Similar results have been reported when the effect of annealing on the conductivity of PANI was investigated [52,53].

3.2. Effect of kinetic variables

3.2.1. Effect of [H₂O₂]

The dependence of reaction rate on the initial concentration of hydrogen peroxide, [H₂O₂]₀, has been investigated. The [dye] and the mass of composite (III) were kept constant at 1×10^{-4} M and 0.02 g, respectively, while the [H₂O₂]₀ was varied in the range 5×10^{-3} to 10×10^{-2} M at 30 °C. Values

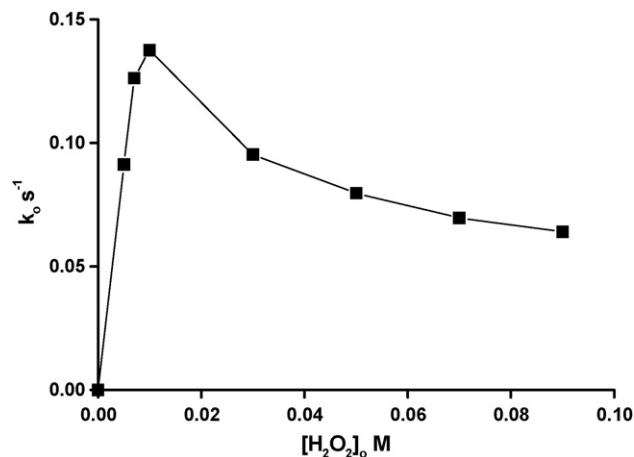


Fig. 7. Variation of the rate constant of the reaction of DR-81 (5×10^{-5} M) with [H₂O₂]₀ in the presence of 0.02 g of composite (III) at 30 °C.

of k at different $[\text{H}_2\text{O}_2]_0$ were determined. They increased with the increase in $[\text{H}_2\text{O}_2]_0$ attaining a maximum at *ca.* 0.01 M and thereafter decreased (Fig. 7). This behavior may be explained on the basis of the adsorption of H_2O_2 onto the active PANI centers. These centers are the quinoid rings of the ES form of PANI. Since the number of centers would be limited because the mass of composite was kept constant (0.02 g), but the $[\text{H}_2\text{O}_2]$ was increased. The catalytic reaction is assumed to be the reduction of ES form to the EB form with simultaneous oxidation of H_2O_2 to HO_2^\bullet . Therefore, the upward part (Fig. 7), may be attributed to the increase in radical concentration with increasing $[\text{H}_2\text{O}_2]_0$. This increases the probability of the organic molecules attack by HO_2^\bullet which causes an increase in the oxidation rate. The downward part could be attributed to (i) the well-known free radicals scavenging effect via the reaction of free radicals with excess H_2O_2 [54]. (ii) The limiting number of active centers on the catalyst surface comparing with increasing number of H_2O_2 molecules. (iii) The progressive fall in relative efficiency of HO_2^\bullet to oxidize dye molecules. Such factors can reduce the probability of attacking the organic molecules by radicals and consequently the oxidation rate drops. These results suggest that such reaction may represent an efficient method to treat wastewater containing organic dyes using dilute solution of H_2O_2 .

3.2.2. Effect of [dye]

The effect of substrate concentration is important both from the mechanistic and application point of view. Thus, $[\text{H}_2\text{O}_2]$ and the mass of composite (III) were kept constant at 7×10^{-3} M and 0.02 g, respectively, while the [dye] was varied in the range 3×10^{-5} to 1×10^{-4} M. Values of k decreased with increasing the [DR-81] from 3×10^{-5} M to 5×10^{-5} M. Further increase in the [DR-81] led to almost constant rate of reaction. While for AB-92 and IC dyes the k were found to decrease continuously with increasing the substrate concentration from 3×10^{-5} M to 1.2×10^{-4} M (Fig. 8). The presumed reason is that when the [dye] increases, more molecules are adsorbed on the surface of PANI/MnO₂ composite. The large amount of adsorbed dye is thought to have

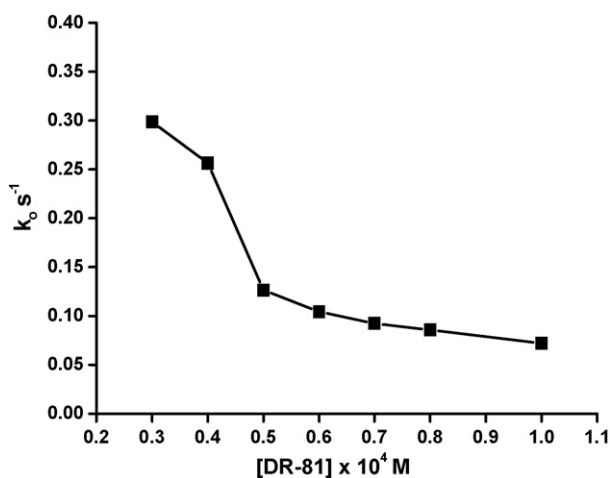


Fig. 8. Dependence of the reaction rate on [DR-81], $[\text{H}_2\text{O}_2] = 7 \times 10^{-3}$ M in the presence of 0.02 g of the composite (III) at 30 °C.

an inhibiting effect on the generation of free radicals species, due to the retardation of the interaction between H_2O_2 and PANI/MnO₂. According to the value of zero point of charge of the composite (pH 3), its surface is presumably positively charged. On the other hand, the dyes have negatively charged sulfonic acid groups. Thus, the adsorption process via electrostatic interaction becomes favorable.

3.2.3. Effect of the amount of composite

The kinetic measurements were carried out at $[\text{dyes}] = 1 \times 10^{-4}$ M and 0.5×10^{-4} M for (AB-92 & IC), and DR-81, respectively, $[\text{H}_2\text{O}_2]_0 = 7 \times 10^{-3}$ M, while the amount of the composite (III) was varied in the range 0.01–0.05 g. Experiments performed with different amount of PANI/MnO₂ showed that the oxidation rate increased with increasing the amount of PANI/MnO₂. The rate was enhanced by about 90%, 86%, and 82% for AB-92, DR-81, and IC, respectively, when the amount of the composite changed from 0.01 g to 0.05 g.

3.2.4. Effect of temperature

Temperature is a crucial parameter in most of the catalyzed reactions, particularly those used in environmental and industrial applications. The effect of temperature on the reaction rate was studied by varying the temperature in the range 303–318 K. The plot of $\ln k$ versus $1000/T$ gave a straight line from which the apparent activation energy, E , was determined. This energy and the other activation parameters are depicted in Table 2. A plot of ΔH^\ddagger versus ΔS^\ddagger gave rise to straight line with a slope equals 306 K (isokinetic temperature). This value is smaller than the average experimental value 310.5 K, which means that the activation process is entropy controlled. This linear relationship Fig. 9 provides a good evidence that the oxidative reactions of the present dyes followed the same mechanism [55]. Such phenomenon is supported with that reported in [33,34].

3.2.5. Effect of pH

The effect of pH on the reaction rate was studied at constant [dyes] and $[\text{H}_2\text{O}_2]$ as well as fixed amount of composite (III) at 30 °C. The pH was varied in the range (5.5–11) using the phosphate buffer of 0.067 M. A few drops of NaOH were added to obtain the high pH values. Values of k decreased with pH as shown in Fig. 10. This trend may be ascribed to the following aspects: (i) the measured value of zero point of charge of the composite (pH 3), whereby the number of positive charges decreases with increasing the pH. It has been reported that the rate of pollutants degradation reaches its maximum near the zero point of charge of the catalyst [56,57]. (ii) The deprotonation of ES form of PANI to EB with increasing pH. The EB form was found inactive catalyst in our oxidation system as mentioned previously in Section 3.1.1. (iii) Adsorption of the dye on the composite surface becomes more facile at high pH. (iv) The deprotonation rate of H_2O_2 increases with increasing pH. It is well known that the optimum pH for the formation of free radicals in the Fenton process was in the range 2–3 [40].

Table 2

The rate constants and activation parameters for the oxidative decolorization of the dyes with H_2O_2 (7×10^{-3} M) in the presence of 0.01 g of composite (III)

Dyes	Temperature ($^{\circ}\text{C}$)	k ($\times 10^2 \text{ s}^{-1}$)	E (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)
DR-81	30	12.63	38.44	36.01	80.43	–143.1
	35	14.43				
	40	17.54				
	45	26.07				
IC	30	12.16	34.53	31.96	80.22	–156.3
	35	14.85				
	40	17.83				
	45	23.27				
AB-92	30	12.99	21.10	18.53	80.10	–200.5
	35	14.93				
	40	16.33				
	45	19.32				

3.2.6. Effect of ionic species

The effect of ionic species is worth to be investigated, since the industrial effluents have different salts of wide range of concentrations. The effect of sulfate anions on the reaction rate was studied at fixed [dye], $[\text{H}_2\text{O}_2]$, and constant amount of composite (III), while $[\text{K}_2\text{SO}_4]$ was varied in the range 0.01–0.25 M (data not shown). Values of k determined from first-order plots decreased with increasing $[\text{K}_2\text{SO}_4]$. The inhibiting effect caused by K_2SO_4 can be explained on the basis of (i) the scavenging character of SO_4^{2-} towards the free radical species with the formation of SO_4^{\bullet} radicals [58]. Obviously, SO_4^{\bullet} radical is less active oxidizing agent. (ii) The presence of salt may enhance the aggregation of dye molecules [59]. In contrast, the reaction rate was enhanced upon the addition of KNO_3 in the concentration range 0.05–0.35 M (Fig. 11). This enhancement may be due to (i) the favorable adsorption of NO_3^- on the surface of composite as derived from the TGA analysis [11], the adsorbed NO_3^- may work as dopant anion for PANI. (ii) The formation of nitrate radical NO_3^{\bullet} in the presence of H_2O_2 [60]. The y-intercept of Fig. 11 is in a good agreement with the value of k determined in the absence of NO_3^- ion under comparable conditions.

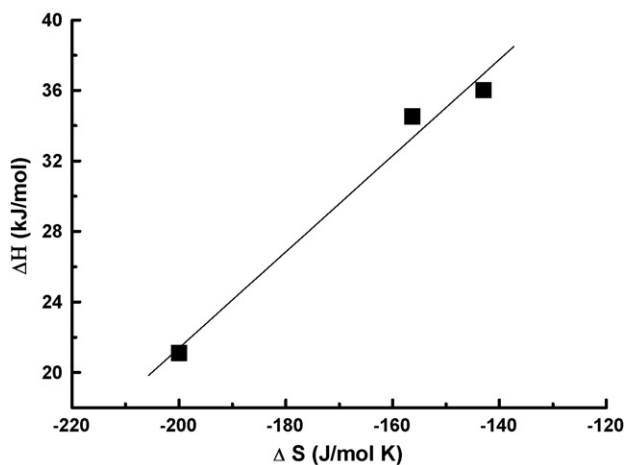


Fig. 9. Isokinetic relationship for the oxidative reaction of the dyes under consideration.

3.2.7. Effect of UV-irradiation

It is well established that the combination of ultraviolet light with H_2O_2 leads to complete degradation of organic dyes [57–59]. Under these conditions, the generation of HO^{\bullet} is well confirmed. When the reaction mixture was irradiated by UV-light of $\lambda = 254$ nm, an enhancement in reaction rate of ca. 80.8%, 78.1% and 85.61% was detected for DR-81, IC and AB-92, respectively. Such enhancement is a good evidence for the generation of free radical species of high concentration upon the UV-irradiation. Similar behavior has been observed elsewhere [33–35].

3.3. Mechanism

Based on the experimental findings and observations, the reaction mechanism has been suggested utilizing the redox properties of H_2O_2 . These properties involve a cyclic electron transfer process, which is initiated either by transfer of an electron from H_2O_2 to the oxidizing sites of the catalyst to produce the HO_2^{\bullet} radical or transfer of an electron from the reduced sites of the catalyst to H_2O_2 to produce HO^{\bullet} [40,54]. The redox mechanism of PANI is also established, based on the

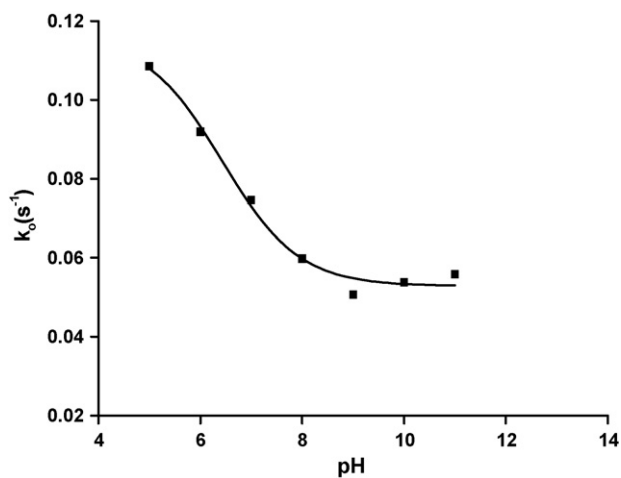


Fig. 10. Variation of the reaction rate constant with pH for the reaction of AB-92 (1×10^{-4} M) with H_2O_2 (7×10^{-3} M) in the presence of 0.02 g of composite (III) at 30°C .

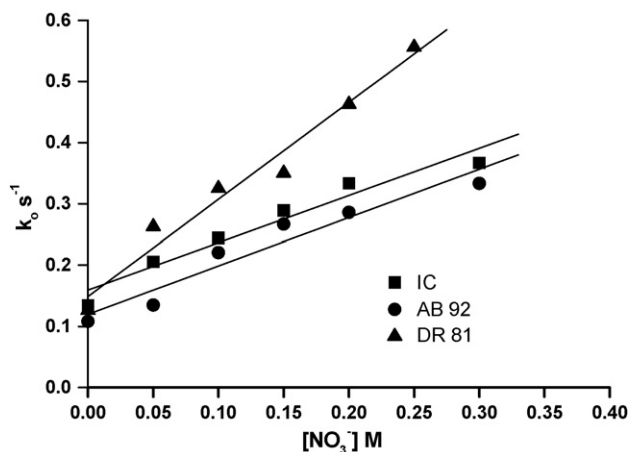
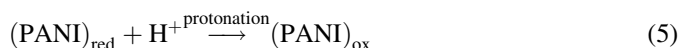
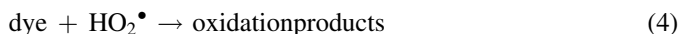
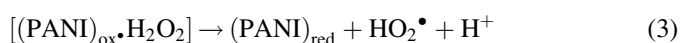
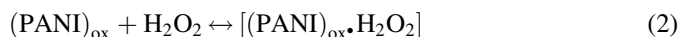


Fig. 11. Variation of the rate constant of the oxidation of chosen dyes with $[\text{NO}_3^-]$ $[\text{H}_2\text{O}_2] = 7 \times 10^{-3} \text{ M}$ in the presence of 0.02 g of composite (III) at 30°C .

thermodynamics of redox processes in homogeneous solutions [61–63]. Nevertheless, the limitation of this system is that its redox activity is valuable only at $\text{pH} < 4$ [54]. Two possible reaction types for the oxidation of the polymer have been proposed: (i) PANI reduction, without degradation of the polymer chains, due to the reversible amine–imine-type transformation. (ii) Redox reaction, which directly modifies the polymer skeleton and then ruptures the chain with its subsequent hydrolysis [64]. In addition to the main role of MnO_2 as oxidant for the preparation of the composite, it offers two important functions: (i) the adsorbed anions, NO_3^- , Cl^- , SO_4^{2-} , and PO_4^{3-} , may compensate the excess positive charges that formed in PANI layers. (ii) The pH of the reaction medium ($3 \approx 4.5$) may be attributed to the adsorption of H^+ on MnO_2 surface. This pH is close to that reported for the Fenton-like reaction of H_2O_2 for the generation of free radical species. (iii) The transformation of MnO_2 into MnOOH after the polymerization process, and the loss of its crystallographic form depress its role in the oxidation reaction. A reaction mechanism involving free radical species, can be proposed as



where $(\text{PANI})_{\text{ox}}$ and $(\text{PANI})_{\text{red}}$ are the ES and EB forms of the polymer. The first step of reaction mechanism is the adsorption of H_2O_2 on the oxidized sites of the polymer, Eq. (2), which is followed by the reduction of oxidized PANI with H_2O_2 to form HO_2^\bullet radical species, Eq. (3). The generated radicals will attack the dye molecules, Eq. (4), to form the reaction products. It is well known the conversion between EB and ES forms of PANI can be occurred by protonation, thus Eq. (5) involves the regeneration of oxidized form of PANI. Identification of the oxidation products is out of the scope of this work.

4. Conclusions

The objective of this study was the investigation of the effects of various parameters changed for the preparation of PANI/ MnO_2 composites on their catalytic activity. The model reactions used are the oxidative decolorization of the three textiles dyes: DR 81, IC, and AB 92 with H_2O_2 as an oxidant. The composites showed superior catalytic activity for complete decolorization of the target dyes within 30 min and strongly depends on the kind of dye. The optimum conditions for maximum decolorization were found to be at (i) high $[\text{ANI}]$, (ii) moderate amount of MnO_2 (2.5 g), (iii) moderate $[\text{acid}] \approx 0.76 \text{ M}$, (iv) low polymerization temperature and (v) using nitric acid as medium. Investigation of the kinetic variables showed that the maximum rates were obtained in the presence of (i) $[\text{H}_2\text{O}_2] \leq 0.01 \text{ M}$, (ii) low concentration of the dye and (iii) acidic medium. This catalytic system offers several advantages such as the inexpensive mass production of the catalyst, short reaction time, and non-toxic reagents which make the reaction simple, elegant and environmentally benign.

Acknowledgements

We are grateful to Dr. M.A. Salem for helpful reading and discussions and Dr. S.A. El-Safty for the X-ray and SEM measurements of composite samples.

References

- [1] J. Anand, S. Palaniappan, D.N. Sathyanarayana, *Prog. Polym. Sci.* 23 (1998) 993.
- [2] O.Y. Posudievsky, S.A. Biskulva, V.D. Pokhodenko, *J. Mater. Chem.* 12 (2002) 1446.
- [3] R.L.N. Chandrakanthi, M.A. Careem, *Thin Solid Films* 417 (2002) 51.
- [4] G.M. Nasciment, V.R.L. Constantino, M.L.A. Temperini, *Macromolecules* 35 (2002) 7535.
- [5] B.Z. Tang, Y.H. Geng, J.W.Y. Lam, B.S. Li, *Chem. Mater.* 11 (1999) 1581.
- [6] M. Biswas, S.S. Ray, Y.P. Liu, *Synth. Met.* 105 (1999) 99.
- [7] J. Sus, N. Kuramoto, *Synth. Met.* 114 (2000) 147.
- [8] S.S. Ray, M. Biswas, *Synth. Met.* 108 (2000) 231.
- [9] L. Peng, L. Weimin, X. Qunji, *Mater. Chem. Phys.* 87 (2004) 109.
- [10] B. Nirmalya, *Mater. Lett.* 58 (2004) 3257.
- [11] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, *Eur. Polym. J.* 41 (2005) 2575.
- [12] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, *J. Colloid Interface Sci.* 308 (2007) 385–394.
- [13] M.J. Croissant, T.L. Napporn, C. Lamy, *Electrochim. Acta* 43 (1998) 2447.
- [14] L. Niu, L. Qiuhong, W. Fenghua, C. Xiao, H. Wang, *Synth. Met.* 139 (2003) 271.
- [15] M. Shaolin, K. Jingjing, *Synth. Met.* 132 (2002) 29.
- [16] Z. Mandic, L.J. Duic, *Electroanal. Chem.* 403 (1996) 133.
- [17] V.G. Khomenko, V.Z. Barsukov, A.S. Katashinskii, *Electrochim. Acta* 50 (2005) 1675.
- [18] R.S. Reddy, S. Das, T. Punniyamurthy, *Tetrahedron Lett.* 45 (2004) 3561.
- [19] J. Haber, M. Klosowski, J. Poltowicz, *J. Mol. Catal. A: Chem.* 201 (2003) 167–178.
- [20] M. Higuchi, I. Ikeda, T. Hirao, *J. Org. Chem.* 62 (1997) 1072.
- [21] T. Kurbus, L.M.A. Majcen, D.B. Voncina, *Dyes Pigments* 58 (2003) 245–252.
- [22] X. Xiang-Rong, L. Hua-Bin, W. Wen-Hua, G. Ji-Dong, *Chemosphere* 57 (2004) 595–600.

- [23] J.T. Spadaro, L. Isabelle, V. Renganathan, *Environ. Sci. Technol.* 28 (1994) 1389–1393.
- [24] M. Styliadi, D.I. Kondrides, X.E. Verykios, *Appl. Catal. B: Environ.* 47 (2004) 189.
- [25] R. Nilsson, R. Nordlinder, U. Wass, *Br. J. Ind. Med.* 50 (1993) 65–70.
- [26] M.K. Sharma, R.C. Sobti, *Mutat. Res.* 465 (2000) 27–38.
- [27] H.Y. Shu, M.C. Chang, *Dyes Pigments* 65 (2005) 25–31.
- [28] H. Kusic, N. Koprivanac, L. Srsan, J. Photochem. Photobiol. A: Chem. 181 (2006) 195–202.
- [29] S. Echigo, H. Yamada, S. Matsui, S. Kawanishi, K. Shishida, *Water Sci. Technol.* 34 (1996) 81.
- [30] A. Balcioglu, I. Arslan, M.T. Sacan, *Environ. Technol.* 22 (2001) 813.
- [31] I.A. Salem, *Appl. Catal. B: Environ.* 28 (2000) 153.
- [32] R. Aplin, T.D. Waite, *Water Sci. Technol.* 42 (2000) 345.
- [33] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, *J. Mol. Catal. A: Chem.* 193 (2003) 109.
- [34] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, *J. Chem. Technol. Biotechnol.* 79 (2004) 85.
- [35] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, *J. Colloid Interface Sci.* 263 (1) (2003) 228.
- [36] P.C. Fung, K.M. Sin, S.M. Tsui, *J. Soc. Dyes Colorist* 116 (2000) 170.
- [37] C. Zwinter, F.H. Krimmel, *Water Res.* 34 (2000) 1881.
- [38] B. Ulusoy, C. Ebrutalkayab, S. Fusun, *J. Hazard. Mater. B* 114 (2004) 159–166.
- [39] S. Amit, G. Rupali, *Desalination* 167 (2004) 55–63.
- [40] C. Flox, S. Ammar, C. Arias, E. Brillas, A. Vargas-Zaval, R. Abdehdi, *Appl. Catal. B: Environ.* 67 (2006) 93–104.
- [41] W. Jia, E. Segal, D. Kornemandel, Y. Lamhot, M. Narkis, A. Siegman, *Synth. Met.* 128 (2002) 115.
- [42] T. Hirao, M. Higuchi, I. Ikeda, Y. Ohshiro, *J. Chem. Soc., Chem. Commun.* (1993) 194.
- [43] P. Ghosh, S.K. Siddhanta, S.R. Haque, A. Chavabarti, *Synth. Met.* 123 (2001) 83.
- [44] M.M. Ayad, N. Salahuddin, M.A. Shenashin, *Synth. Met.* 142 (2004) 101.
- [45] G.M. Morales, M. Liusa, M.C. Miras, C. Barhero, *Polymer* 38 (1997) 5247.
- [46] P. Sbaite, D. Huerta-Vilca, C. Barber, M.C. Miras, A.J. Motheo, *Eur. Polym. J.* 40 (2004) 1445.
- [47] G. Jiantuan, Q. Jiuhui, *Appl. Catal. B: Environ.* 47 (2004) 133.
- [48] Z.M. Zhang, Z.X. Wei, M.X. Wan, *Macromolecules* 35 (2002) 5937.
- [49] M. Vilenik, M.M. Zigon, M. Zupan, A. Sebenik, *Acta Chim. Solvent* 45 (1998) 51.
- [50] Z. Jin, Y. Su, Y. Duane, *Sens. Actuators B* 71 (2000) 118.
- [51] J. Stejskal, A. Riede, D. Hlavata, J. Prokes, M. Helmstedt, *Synth. Met.* 96 (1998) 55.
- [52] E. Erdem, M. Karakisla, M. Sacak, *Eur. Polym. J.* 40 (2004) 785.
- [53] Q. Hong, W. Wei, L. Jing, F. Kun, M. Weiming, *Synth. Met.* 155 (2005) 560.
- [54] J. De Laat, T.G. Le, *Appl. Catal. B: Environ.* 66 (2006) 137.
- [55] G.R. Wilkins, *The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, MA, 1974 p. 101.
- [56] A. Mokhtar, Y.L. Nargess, M.M. Niyaz, S.T. Nooshin, *J. Hazard. Mater.* 135 (2006) 171.
- [57] D. Chen, A.K. Ray, *Water Res.* 32 (11) (1998) 3223.
- [58] K. Ntampegloitis, A. Riga, V. Karayannis, V. Bantozoglou, G. Papapolymerou, *J. Hazard. Mater.* 136 (2006) 75.
- [59] A.A. Yawalkar, D.S. Bhthande, V.G. Panortar, A.A. Beeinakars, *J. Chem. Tech. Biotech.* 76 (4) (2001) 363.
- [60] J.D. Hamlin, D.A.S. Phillips, *Dyes Pigments* 41 (1999) 137.
- [61] W. Lei, N.M. Kocherginsky, *React. Funct. Polym.* 45 (2000) 65.
- [62] L. Duic, M. Kraljic, S. Grigic, *J. Polym. Sci. A: Polym. Chem.* 42 (2004) 1599–1608.
- [63] Lj Duic, S. Grigic, *Electrochim. Acta* 46 (2001) 2795–2803.
- [64] E.M. Genies, A. Boyle, M. Lakowski, C. Tsintavis, *Synth. Met.* 36 (1990) 139.